Supplementary Information for

High-resolution solid-state oxygen-17 NMR of actinide-bearing compounds: an insight into the 5*f*-chemistry

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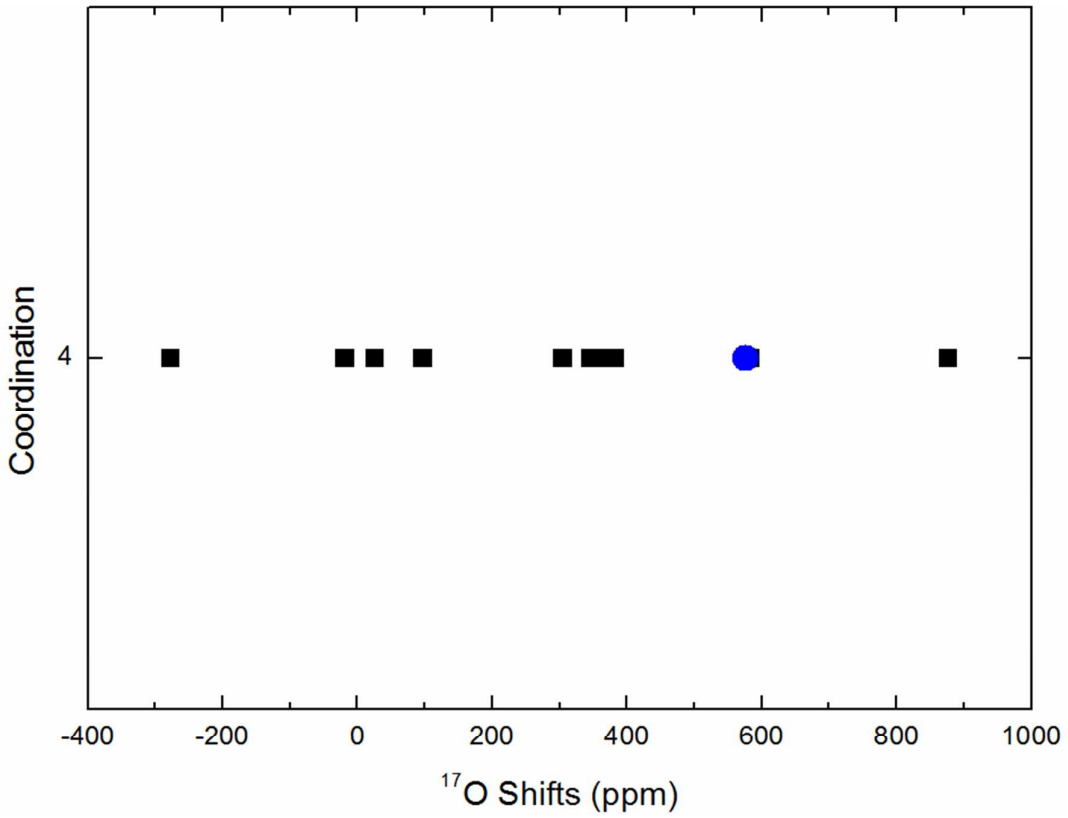

Figure S1: ^{17}O shifts of diamagnetic metal oxides[1] (black squares) compared with that of ThO_2 (blue circle).

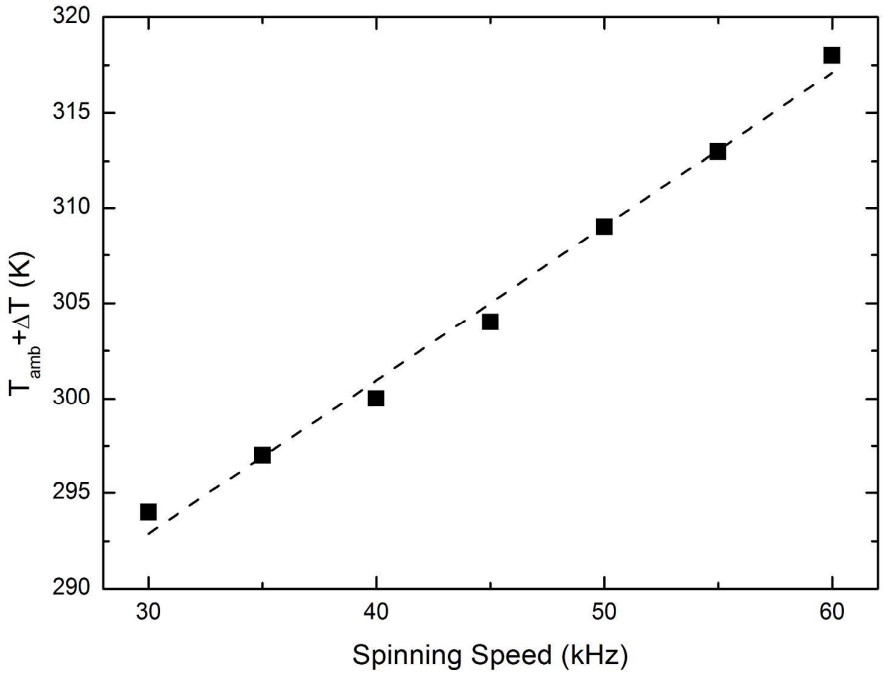

Figure S2: Evolution of the temperature (room temperature (T_{amb}) with a gradient of temperature (ΔT)) with increasing spinning speed. The temperatures have been determined using $Pb(NO_3)_2$ correlations[2] The dashed line is a linear fit.

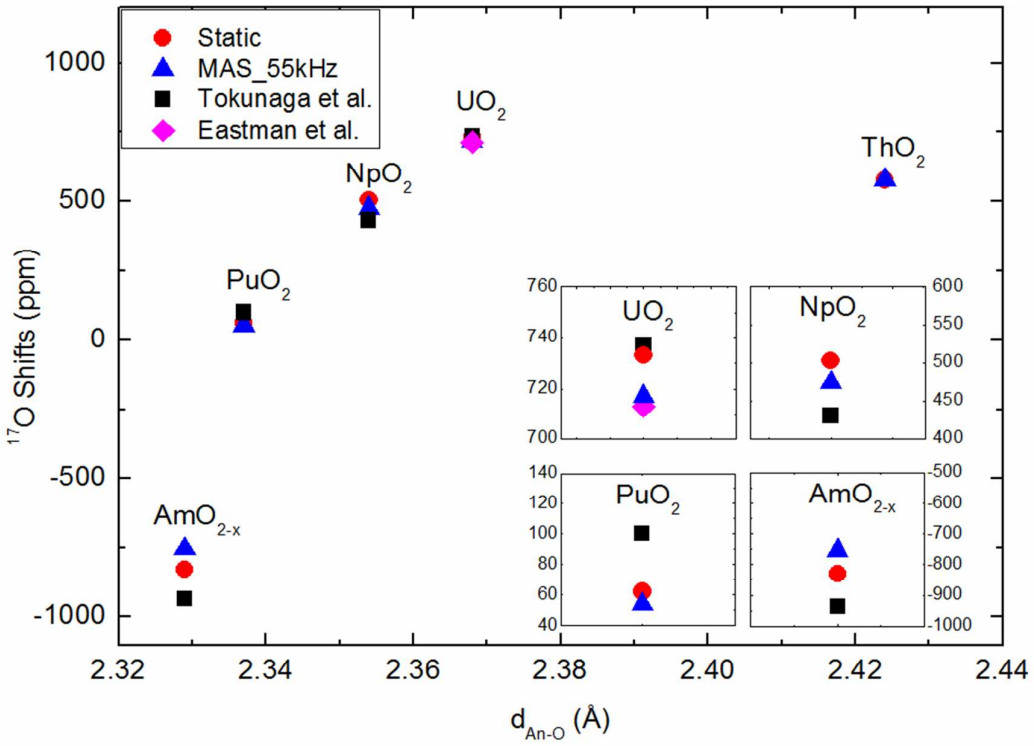

Figure S3: Evolution of the ^{17}O shift as a function of the An-O distance. The results obtained in this study (static and MAS at 55 kHz) are compared with the previous static experiments published by Tokunaga et al.[3] (black squares) and Eastman et al. (pink diamond) [4]. The insets give a better view to compare the ^{17}O shifts of each sample obtained in this study and by the other authors.

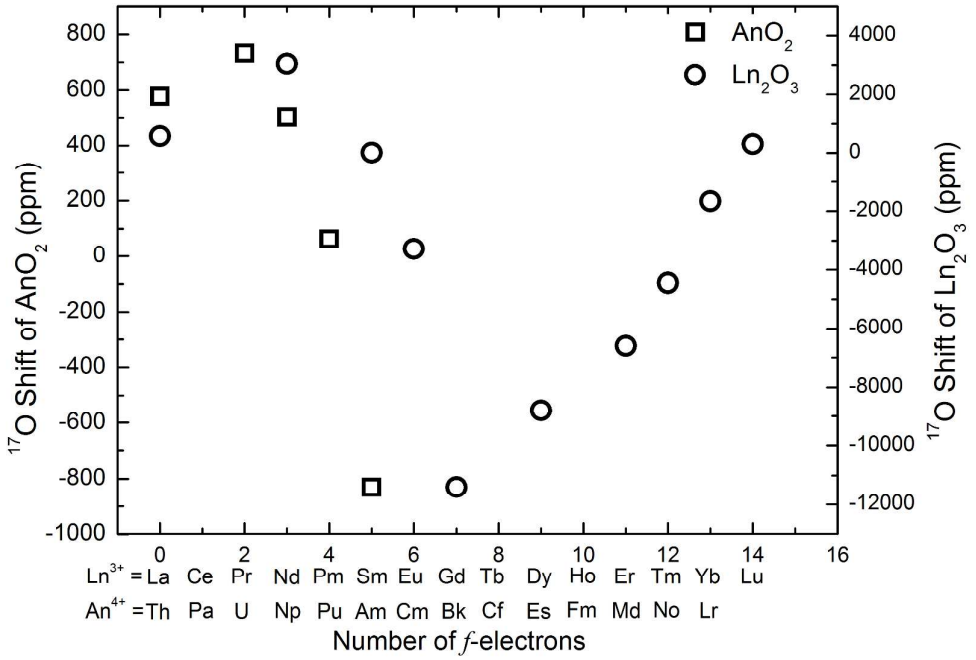

Figure S4: Evolution of the ^{17}O chemical shifts in lanthanide (Ln_2O_3) (from reference 5) and actinides (AnO_2) dioxides as a function of the number of *f*-electrons.

Table S1: B_4 and B_6 are the crystal field (CF) parameters which appear in H_{CF} (see Equation 4 in main text), and are taken from the given literature references. $A\langle S_z\rangle$ is calculated in several different ways to show the relevant trends: RS = Russell-Saunders coupling, no CF (i.e. only the lowest pure $^{2S+1}L_J$ manifold is accounted for without removing its zero-field degeneracy); IC = Intermediate coupling, no CF (i.e. H_{FI} is diagonalized in order to take into account the mixing of excited $^{2S'+1}L'_J$ manifolds into the ground one, which remains 2J+1-fold degenerate in zero field); RS+CF = H_{CF} is diagonalized within the lowest pure $^{2S+1}L_J$ manifold, and $A\langle S_z\rangle$ is calculated as a thermal average over the so-obtained wavevectors; IC+CF = H_{FI} + H_{CF} is diagonalized over the whole $5f^n$ configuration states, and $A\langle S_z\rangle$ is calculated as a thermal average over the so-obtained wavevectors. The results of the latter computational scheme are those presented in Figure 5.

Name	B_4 (cm^{-1})	B_6 (cm^{-1})	$A\langle S_z\rangle$ (RS)	$A\langle S_z\rangle$ (RS+CF)	$A\langle S_z\rangle$ (IC)	$A\langle S_z\rangle$ (IC+CF)
ThO_2			0	0	0	0
UO_2	-7950	3400	-3.20	-2.90	-2.24	-2.12
NpO_2	-8500	3400	-4.91	-4.42	-3.13	-2.97
PuO_2	-9750	4000	-4.80	-4.59	-1.12	-1.46
AmO_2	-2200	–	-1.79	-1.97	-1.70	-0.14

References

1 K. J. D. Mackenzie and M. E. Smith, Multinuclear Solid-State NMR of Inorganic Materials, *Pergamon Materials Series*.

2. Bielecki, A.; Burum, D.P. *J. Magn. Reson. A*, **116**, 215–220 (1995).

3. Tokunaga, Y., et al. NMR studies of actinide dioxides. J. Alloys Compd., **444–445**, 241–245 (2007).

4. Eastman, M. P.; Hecht, H. G.; Lewis, W. B. *J. Chem. Phys.* **54**, 4141-4146 (1971).

5. Yang, S.; Shore, J.; Oldfield, E. *J. Magn. Reson.*, **99**,408-412 (1992).